# <sup>40</sup>Ar/<sup>39</sup>Ar STEP HEATING LASER SYSTEM DATING OF ZINNWALDITE AND MUSCOVITE FROM TIN DEPOSITS OF THE RONDÔNIA TIN PROVINCE, BRAZIL: EVIDENCE FOR MULTIPLE MINERALIZATION EPISODES

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#### INTRODUCTION

Tin mineralization in the Rondônia Tin Province (RTP), has been responsible for over 250,000 t Sn, making this region one of the most productive tin-mining province in the world. The primary tin mineralizations are related to three youngest rapakivi granite suites: the São Lourenço-Caripunas Intrusive Suite (1.31–1.30 Ga), Santa Clara Intrusive Suite (1.08–1.07 Ga) and Younger Granites of Rondônia (1.00–0.97 Ga) (Bettencourt *et al.*, 1999). U-Pb dating on cassiterite appears worldwide difficult in spite of a few results so far obtained (e.g.: Andrew *et al.*, 1992; Sparrenberger & Tassinari, 1999; and others). We have previously reported on Rb-Sr and K-Ar indirect dating of mica from tin granites and greisen (Priem *et al.*, 1971; 1989; Leite Jr. *et al.*, 2001), though they show high discrepancies in relation to the most probable ages of cassiterite crystallization.

This ongoing study has been conducted in three tin-polymetallic deposits: the Santa Bárbara, Bom Futuro and Potosi (Fig.1) and presents, for the first time, new measurements of <sup>40</sup>Ar/<sup>39</sup>Ar spectra on single zinnwaldite and muscovite crystals. This constitutes a new test of obtaining detailed geochronological information, and the Ar/Ar plateau ages of are used to investigate the timing of each style of mineralization, and also to examine the duration of the hydrothermal event that pervasively altered the host rocks. Moreover, it is expected that the results will contribute to the correct interpretation of the K–Ar and Rb–Sr ages of the mineralized host rocks.

# MINERALIZATION STYLES

The Santa Bárbara deposit is hosted by the the Santa Bárbara massif ( $993 \pm 5$  Ma and  $989 \pm 13$  Ma, U-Pb monazite; Sparrenberger *et al.*, 2002), which is part of the Younger Granites of Rondônia. The tin mineralization in the Santa Bárbara mine covers an area of 500 by 150 m, is hosted within a porphyritic to equigranular albitemicrocline granite (apical part of the cupola), and is characterized by two main styles of mineralization: 1) horizontal to sub-horizontal lens-shaped cassiterite-bearing topaz-zinnwaldite-quartz greisen bodies (up to 40 m thick); and 2) a vein-veinlet/stockwork, encompasing brittle zones containing topaz-zinnwaldite-quartz greisen veins with cassiterite-wolframite, quartz-cassiterite veins, muscovite veins, and late kaolinite stockwork/veinlets (Sparrenberger & Bettencourt 2000; Sparrenberger, 2003).

Information on the Potosi Hill deposit (now largely exhausted) relies on the papers of Kopershoek *et al.* (1980), Bettencourt *et al.* (1981), and Yokoi *et al.* (1987). The primary deposit occupies an area of 220 x 280 m in area, and is formed mainly by a Sn–W mineralized exogreisen body (breccia pipe), formerly exposed for a vertical distance of 178 m, and hosted by biotite and biotite hornblende gneisses of the old basement rocks of the Jamari complex (1.75 Ga). The primary exogreisen was brecciated, and the open spaces filled with topazite. All the previous rocks were overprinted by a later sulfide mineralization stage represented by sulfide-bearing quartz veins. Stockworks of greisen veins and veinlets hosted by gneissic country rocks are noticed, outside the main mineralized orebody.

The Bom Futuro mine involves two adjacente hills: the Palanqueta hill (at north) and the Bom Futuro hill (at south), the later being responsible for the larger tin production of the mine. The deposit consists of two breccia pipes, hosted in gneisses and amphibolites of the basement complex, which are crosscut by dykes of topaz-bearing granite porphyries, and pegmatite and quartz veins, according to the following sequence: topaz-bearing rhyolite porphyry—pegmatite—topaz-bearing granite porphyry—quartz vein. The pegmatite and quartz veins constitute the main styles of primary tin mineralization, which have been assigned to the Younger Granites of Rondônia.

# MATERIALS AND METHODS

The present study has been undertaken on samples of Li–Fe micas, which were classified as zinnwaldite according to Rieder *et al.* (1998) and Lowell & Martin (1997), and muscovite (Sparrenberger, 2003). In the Santa Bárbara mine three samples of zinnwaldite (AM-52, AM-145, AM-35) were picked from syenogranite, albite-microcline granite and bedded greisen, respectively, and one muscovite (AM-37) from a late muscovite vein. Two zinnwaldite samples from the Bom Futuro Mine (BF-57E, BF-59B) were collected, respectively, from a pegmatite and later quartz vein, which crosscut all the mineralization types. One sample of muscovite was

taken from the primary mica greisen of the Potosi Mine. The samples were crushed and reduced to 40-100 mesh grain size. Mica separation was completed on a Frantz Isodynamic Magnetic Separator, and depending on the mica composition, after the initial rough elimination of all other minerals, two or three final separations at 0.3 or 0.25 A were used to exclude mica flakes aggregated with other minerals, in order to obtain high purity mica concentrates. These were subsequently cleaned in ultrasonic bath during 20 minutes. Grains smaller than 2.1 mm were analyzed. The argon geochronology was carried out at the CPGeo Argon Lab (IGUSP), which facilities are divided into two major units: 1) a home-built fully automated noble gas stainless steel ultra-high vacuum gas extraction and purification system, coupled with a continuous laser; 2) the MAP-215-50 mass-spectrometer. Five to ten grains from each sample were loaded into the disks along with Fish Canyon sanidine standards (28.02  $\pm$  0.28 Ma; Renne *et al.*, 1998). The disks were wrapped in Al-foil, sealed in silica glass tubes and irradiated for 30 hours at the IPEN/CNEN IEA-R1 nuclear reactor, São Paulo, Brazil (Vasconcelos *et al.*, 2002).

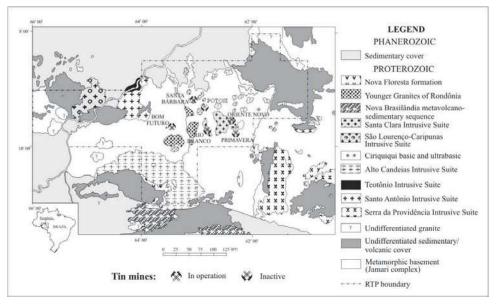


Figure 1 - Simplified geological map of the Rondônia Tin Province and adjacent areas (modified from Bettencourt et al., 1999).

Three mica grains of each sample were analyzed via laser incremental heating. The argon isotopes ratios (\frac{40}{40}Ar/\frac{39}{40}Ar, \frac{38}{40}Ar/\frac{39}{40}Ar, \frac{36}{40}Ar/\frac{39}{40}Ar, the

percentage of radiogenic argon (40Ar\*), the age obtained for each incremental heating step, J factors, laser beam intensity,  $^{40}$ Ar/ $^{36}$ Ar discrimination, correction factors, and full system blanks were performed. Isotopic run data were corrected for mass discrimination, radioactive decay and nucleogenic interferences. The decay constants recommended by Steiger & Jager (1977) were used. All errors are  $2\sigma$ .

# <sup>40</sup>Ar/<sup>89</sup>Ar dating results

Zinnwaldite and muscovite are common hydrothermal minerals in paragenesis with cassiterite in all the mining district settings of the RTP. Argon–Argon plateau ages of these minerals were used to investigate the timing of each type of mineralization. The isotopic ratio and apparent ages are reported in the Table 1. For the sake of comparison and interpretation of the results, the Ar–Ar dates were combined with previous published K–Ar isotopic analyses on Li–Fe micas of greisens and quartz veins, and K–Ar and U–Pb zircon ages of selected granite facies of the tin-granites are presented in Tables 1 and 2, and Fig. 2.

In the Santa Bárbara mine the analyses were performed on two samples of zinnwaldite from a syenogranite (AM-52), and from a highly differentiated albite-microcline-granite (AM-145). Both display well defined plateau ages of  $990 \pm 5$  and  $985 \pm 4$  Ma, respectively. One zinnwaldite sample from the bedded greisen mineralization, over the tin-granite cupola (AM-35), yields young plateau age of  $959 \pm 4$  Ma, and a muscovite from a late dilation fracture-hosted muscovite-vein mineralization (AM-307) yields plateau age of  $987 \pm 1.9$  Ma. In the Bom Futuro mine, single grains of zinnwaldite (BF-57E) from a late fracture-controled pegmatite, and zinnwaldite (BF-59B) from a late quartz vein, which crosscut all the previous rocks, yield plateau ages of  $994 \pm 3$  and  $993 \pm 3$  Ma, respectively. One muscovite sample (PO-1216/22) associated with the primary exogreisen of the Potosi mine, gives a plateau weighted-mean age of  $1053 \pm 3$  Ma.

It is considered that the  $^{40}$ Ar/ $^{39}$ Ar plateau ages from the hydrothermal zinnwaldite and muscovite are closure ages, which reflect cooling through a blocking  $\Delta T$ , and represent the minimum constraints of the Santa Bárbara, Potosi and and Bom Futuro styles of tin mineralization.

Table 1 -  ${}^{40}Ar - {}^{39}Ar$  laser spot fusion analytical data.

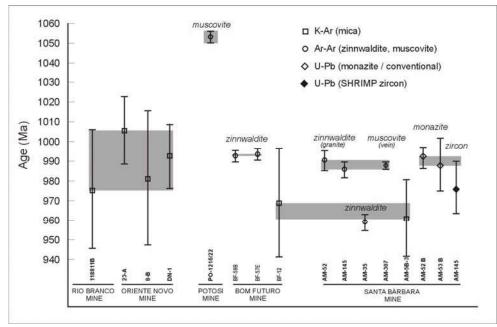
Mine	Sample	Mineral	Rock facies	Age (Ma)
	AM-52	zinnwaldite	syenogranite	990 ± 5
Santa Bárbara	AM-145	zinnwaldite	albite-microcline granite	985 ± 4
	AM-35	zinnwaldite	bedded greisen	959 ± 4
	AM-307	muscovite	muscovite vein	$987 \pm 1.9$
Bom Futuro	BF-57 E	zinnwaldite	pegmatite	994 ± 3
	BF-59 B	zinnwaldite	quartz vein	993 ± 3
Potosi	PO-1216/22	muscovite	mica greisen	$1053 \pm 3$

#### DISCUSSION

In the Santa Bárbara mine, zinnwaldite from bedded greisen (AM-35), yields an unrealistic plateau age, which is significantly younger than the K–Ar mica ages obtained from quartz veins and greisens from the Bom Futuro and Santa Bárbara mines, and also younger than the muscovite (AM-307) from a late-stage muscovite vein. This is not consistent with the field relations between the two styles of mineralization providing that the later crosscut all the previous mineralization styles. This relatively young age probably represents either a protracted cooling history or thermal/chemical resetting, and not an age of crystallization of zinnwaldite. Also the zinnwaldite is F-enriched (up to 5wt %), and the replacement of OH<sup>-</sup> by F<sup>-</sup> and/or Cl<sup>-</sup> has a significant effect upon the thermal stability and other physical properties of trioctahedral micas. In adition the F/Cl ratio (~108) of sample AM-35 is significantly higher (~2.5 x) than the other samples, which may also be an explanation for the anomalous age of sample AM-35. The  $^{40}$ Ar/ $^{39}$ Ar plateau ages of 990 ± 5, 985 ± 4, and 987 ± 1.9 Ma from the Santa Bárbara mine, and of 994 ± 3 and 993 ± 3 Ma from Bom Futuro mine, are slightly at the limit of published U–Pb age estimates for emplacement of the Santa Bárbara massif and Bom Futuro late-stage tin-granites. However, these Ar–Ar plateau ages are ~29 to 25 Ma older than the corresponding K–Ar ages for the Li–Fe micas of greisens and quartz veins from both mines (961 ± 19 and 969 ± 27 Ma, respectively).

Figure 2 - Variation range of  $^{40}Ar/^{39}Ar$ , K-Ar, and U-Pb ages from the Oriente Potosi, Novo, RioBranco and Santa Bárbara tin deposits and associated tingranites, ofthe Rondônia TinProvince.

The distinct plateau age of  $1053 \pm 3$  Ma from the Potosi Mine may represent the minimum mineralization age related to the Santa Clara Intrusive Suite (1.08-1.07 Ga). Also



it is important to remark that the K-Ar ages of greisen and quartz veins from the Santa Clara Intrusive Suite (Leite Jr. *et al.*, 2001), now taken as representing the time of cooling of the hydrothermal granite system, are significantly younger (by  $\sim$ 47 to 77 Ma) than the corresponding Ar-Ar age of  $1053 \pm 3$  Ma.

# **CONCLUSIONS**

The precise <sup>40</sup>Ar-<sup>39</sup>Ar dating of Li-Fe micas suggest that tin mineralization took place early in the cooling history of the late-stage highly evolved rapakivi fluorine rich peraluminous alkali-feldspar granites from the Santa Clara Intrusive Suite and Younger Granites of Rondônia.

The conventional K-Ar ages obtained after Li-Fe micas from the morpho-structural types of mineralization related to the tin-granites may record a slow cooling rate following the tin mineralization episodes.

The preliminary results allow the reconstitution and timing of the hydrothermal activity, providing that further investigations are needed.

Table 2 - K—Ar isotope data on Li-Fe mica from the morpho-genetic types of tin mineralization related to the Santa Clara Intrusive Suite and Younger Granites of Rondônia.

Rock	Sample	Sample Location	K-Ar Age (Ma)	Reference			
SANTA CLARA INTRUSIVE SUITE (1080–1070 Ma; U–Pb zircon age)							
greisen	23-A	Oriente Novo mine	1006 ± 17	Leite Jr. et al.			
greisen	8-B	Oriente Novo mine	981 ± 35	(2001)			
quartz vein	DN-1	Oriente Novo mine	993 ± 16				
greisen	1188-11B	Rio Branco mine	$976 \pm 30$				
biotite-topaz -quartz rock	RON-6	Oriente Novo mine	995 (max. error at ± 4%)	Priem et al. (1971)			
YOUNGER GRANITES OF RONDÔNIA (1000–970 Ma; U–Pb conventional zircon age)							
greisen	5B-3	Santa Bárbara mine	961± 17	Leite Jr. et al.			
				(2001)			
quartz vein	BF-12	Bom Futuro mine	$969 \pm 27$	Leite Jr. et al.			
				(2001)			

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